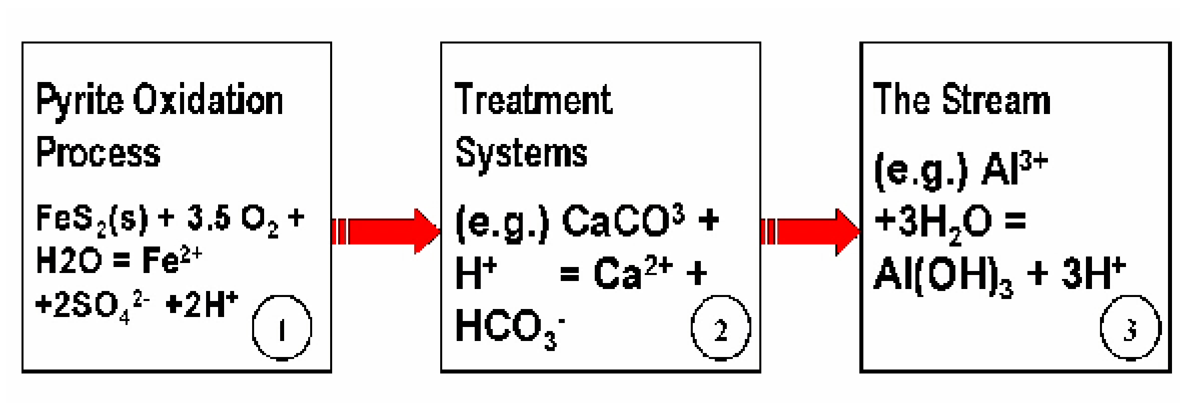
Appendix D

Modeling pH for TMDL Development

Overview

Streams affected by acid mine drainage often exhibit high metals concentrations (specifically for iron [Fe], aluminum [Al], and manganese [Mn]) along with low pH. The relationship between these metals and pH provides justification for using metals TMDLs as a surrogate for a separate pH TMDL calculation. The following figure shows three representative physical components that are critical to establishing this relationship.



Note: Several major ions comprise the water chemistry of a stream. The cations are usually Ca^{2+}, Mg^{2+}, Na^+, K^+, and H^+, and the anions consist of HCO_3^-, CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}, and OH^- (Stumm and Morgan, 1996).

Component 1 describes the beginning oxidation process of pyrite (FeS_2) resulting from its exposure to H_2O and O_2. This process is common in mining areas. The kinetics of pyrite oxidation processes are also affected by bacteria (Thiobacillus ferrooxidans), pH, pyrite surface area, crystallinity, and temperature (PADEP, 2000). The overall stoichiometric reaction of the pyrite oxidation process is as follows:

$$FeS_2(s) + 3.75\ O_2 + 3.5\ H_2O \qquad Fe(OH)_3\ (s) + 2SO_4^{2-}\ + 4H+$$

Lower pH and higher metals concentrations from Component 1 should be treated effectively with applicable systems.

Component 2 presents an example chemical reaction occurring within a mining treatment system.

Examples of treatment systems include wetlands, successive alkalinity producing systems, and open limestone channels. Carbonate and other bases (e.g., hydroxide) created in treatment systems consume hydrogen ions produced by pyrite oxidation and hydrolysis of metals, thereby increasing pH. The increased pH of the solution will precipitate metals as metal hydroxides. Treatment systems may not necessarily work properly, however, because the removal rate of metals, and attenuation of pH depends on chemical constituents of the inflow, the age of the systems, and physical characteristics of the systems (e.g., flow rate, detention rate) (West Virginia University Extension Service, 2000).

It is assumed that implementation of TMDLs in the Tygart watershed for aluminum, iron, and manganese will result in in-stream metals concentrations meeting the water quality criteria. This assumes that treatment systems are implemented properly and effectively increase pH, in order to precipitate and thus lower metals concentrations.

After treatment, the focus shifts to Component 3 and the relationship between metals concentrations and pH in the stream. The chemical process that needs to be considered is the hydrolysis reaction of metals in the stream. Component 3 presents an example of this reaction. In order to estimate pH resulting from chemical reactions occurring in the stream, MINTEQA2 (a geochemical equilibrium speciation model for dilute aqueous systems) was used.

MINTEQA2 Application

MINTEQA2 is an EPA geochemical equilibrium speciation model capable of computing equilibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation states, and precipitation-dissolution of metals in an environmental or lab setting. The model includes an extensive database of reliable thermodynamic data. The MINTEQA2 model was run using the following inputs:

Species	Input Values (mg/L)
Ca	43.2
Mg	14.5
Na [a]	6.3
K [a]	2.3
Cl [a]	7.8
SO_4	86.6
Fe [b]	1.5 and 0.5
Al [b]	0.75
Mn [b]	1.0
Alkalinity	18.0 (as $CaCO_3$)

[a] source: Livingstone (1963)
[b] allowable maximum concentrations (TMDL endpoints)

Input values for Fe, Al, and Mn were based on TMDL endpoints (maximum allowable limits). The alkalinity value was based on average in-stream concentrations for rivers relatively unimpacted by mining activities in the Tygart Valley River watershed. Mean observation values were used for the remaining ions requiring input for MINTEQA2. Where observation data were not available, literature values were used for the chemical species. The model was additionally set to equilibrium with atmospheric CO_2. Based on the inputs presented, the resultant equilibrium pH was estimated to be 7.74 using the aquatic life standard (1.5 mg/L total Fe) and 7.76 using the trout waters standard (0.5 mg/L total Fe).

The model was also run using typical in-stream metals concentrations found in the vicinity of mining activities (10 mg/L for total Fe, 10 mg/L for Al, 5 mg/L for Mn, and 3 mg/L as $CaCO_3$ for alkalinity). These inputs resulted in an equilibrium pH of 4.38.

Results from MINTEQA2 imply that pH will be within the West Virginia criteria of above 6 and below 9, provided that in-stream metals concentrations simultaneously meet applicable water quality criteria.

Assumptions

The conclusions presented above assume that TMDLs are implemented properly, so that metals concentrations from point and nonpoint sources result in the stream meeting metals criteria (implying that pH from these sources has already been increased, in order to decrease metals). Additional assumptions (and facts) that were considered in this process are as follows:

Iron (Fe)

Ferric iron was selected as total iron based on the assumption that the stream will be in equilibrium with the atmospheric oxygen. Since iron exhibits oxidized and reduced states, the redox part of the iron reactions may additionally need to be considered. The reduced state of iron, ferrous iron, can be oxidized to ferric iron through abiotic and biotic oxidation processes in the stream. The first process refers to oxidation by increasing the dissolved oxygen because of the mixing of flow. The other process is oxidation by microbial activity in acidic conditions on bedrock (Mcknight and Bencala, 1990). Photoreduction of hydrous oxides also can increase the dissolved ferrous form. This reaction could increase pH of the stream followed by oxidation and hydrolysis reactions of ferrous iron (Mcknight, Kimball and Bencala, 1988). Since water quality data are limited, the concentration of total Fe was assumed to be constant at 1.5 mg/L, and it was assumed that total Fe increase by photoreduction would be negligent. (This assumption could ignore pH changes during daytime.)

Sodium (Na), Potassium (K), and Chloride (Cl)

The concentration of Na, K, and Cl can be higher in streams affected by acid mine drainage. These ions are conservative and are not reactive in natural water, however, so it is likely that the pH of the stream would not be affected.

Calcium (Ca), Magnesium (Mg)

These ions may have higher concentrations than the values used for the modeling in this study due to the dissolution of minerals under acidic conditions and the reactions within treatment systems. Increasing the concentrations of these ions in the stream, however, could result in more complex forms with sulfate in the treatment system and in the river. This should not affect pH.

Manganese (Mn)

Manganese oxide (MnO_2) can have a redox reaction with ferrous iron and produce ferric iron (Evangelou, 1998). This ferric iron can go through a hydrolysis reaction and produce hydrogen ions, thereby decreasing pH.

Biological Activities

Biological activities such as photosynthesis, respiration, and aerobic decay can influence the pH of localized areas in the stream. Biological reactions such as the one below:

$$1/6\ C_6H_{12}O_6 + O_2 \quad CO_2 + H_2O$$

will assimilate CO_2 during photosynthesis and produce CO_2 during respiration or aerobic decay. Reducing CO_2 levels will increase the pH and increasing CO_2 levels will lower the pH of the water (Langmuir, 1997). It is possible that as a result of these biological activities, the pH standards may be violated even though metals concentrations are below in-stream water quality standards.

Kinetic Considerations

The kinetic aspect of metal reactions in the stream is an important factor that also needs to be considered. For example, Fe and Mn can be oxidized very rapidly if the pH of the solution is 7.5 to 8.5; otherwise the oxidization process is much slower (Evangelou, 1995). Having a violation of metals concentrations, but no pH violation might be a result of the kinetic aspect of the reactions.